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EP 0136900 A1 WO 95/12021 A1

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INT CL⁶ A01N 47/44 , D06M 11/11 11/55 13/432

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(54) **Treatment of cellulose with polymeric biguanides**

(57) A cellulosic substrate is treated with a polymeric biguanide followed by an antibonding agent eg. urea or an inorganic acid, to confer anti-microbiological properties to the cellulosic substrate and also to reduce the propensity to yellow on contact with chlorine-containing bleaching agents.

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PROCESS

The present invention relates to a method of treating cellulosic substrates, including their blends, with an antimicrobial polymeric biguanide to give improved resistance to laundering in the presence of anionic detergents and hypochlorite bleach.

It has been proposed to treat textile materials with poly(hexamethylene biguanide) in order to confer antimicrobial properties to the textile material as disclosed in EP 136 900. Polymeric biguanides are particularly suited for application to cellulosic substrates, especially cellulosic textiles, and blends thereof, because of the substantivity which polymeric biguanides exhibit for such substrates. However, such applications have not become commercially established where the treated material is to be subjected to laundering. There are two major reasons for this. Firstly, many commercially available detergents contain chlorine bleaching agents which react with the biguanide groups to produce a yellow discoloration and cause loss of antimicrobial protection. This is a particular disadvantage in white or pale coloured textiles. Secondly, many commercial detergents contain anionic surfactants which can complex with the biguanide groups to produce sticky deposits resulting in loss of "handle" and often impairment of stain-release properties of the textile material. Laundering can also increase the "tendering" of the textile material.

The high substantivity of polymeric biguanides for cellulosic substrates is believed to be due to attraction/interaction between the imino residues of the biguanide groups and oxygen atoms in the cellulose chains. It is also believed that the yellowing which occurs on treating cellulose containing a polymeric biguanide with hypochlorite bleach is due to the formation of chloramines by the imino groups of the biguanide units.

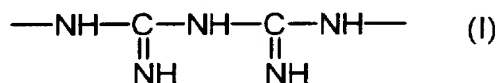
Polymeric biguanides (hereinafter PG) generally consist of mixtures of polymeric and oligomeric species of varying chain lengths having from about 2 up to about 40 biguanide units. The most widely used polymeric biguanide is poly(hexamethylene biguanide) which is available commercially as an aqueous solution of polymeric and oligomeric species in the form of their hydrochloride salts (hereinafter PHMB). The preparation of PHMB is described in GB 702,268 and GB 1,152,243.

We have now found that the yellowing of the cellulosic substrate containing PG when treated with hypochlorite bleach is mainly attributable to oligomers of relatively short chain length and that this yellowing may be significantly reduced by treating the cellulosic substrate containing PG with an anti-bonding agent (hereinafter

ABA) which reduces the substantivity of the relatively short-chain oligomers (especially oligomeric species containing up to 5 biguanide units) for the cellulosic substrate.

According to the invention there is provided a method for treating a cellulosic substrate with PG and thereafter treating the cellulosic substrate containing absorbed PG with an ABA.

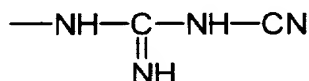
The PG which are used to treat the cellulosic substrate contain at least two biguanide units of the formula (I):-



and preferably from 2 to 40 such biguanide units.

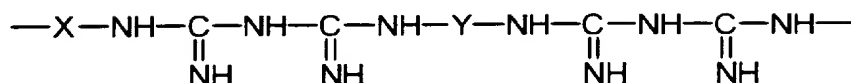
Typically the biguanide units are linked by a bridging group which includes at least one methylene group. The bridging group may include a polymethylene chain which may optionally be interrupted by hetero atoms such as oxygen, sulphur or nitrogen. The bridging group may include one or more cyclic nuclei which may be saturated or unsaturated. It is generally preferred that the bridging group is such that there are at least three, and especially at least four, carbon atoms directly interposed between adjacent units of the formula (I). In general it is preferred that there are not more than ten carbon atoms and, especially not more than eight carbon atoms interposed between two adjacent units of the formula (I).

The terminal biguanide units may themselves be terminated by any suitable terminating group such as hydrocarbyl, substituted hydrocarbyl group, amino or amine hydrochloride or a group



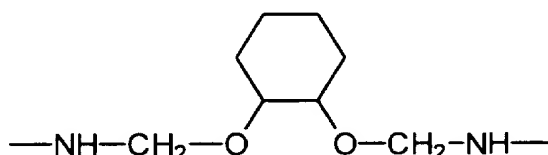
If the terminating group is hydrocarbyl this may be alkyl, cycloalkyl or aryl or a combination thereof, such as aralkyl. If the terminating group is substituted hydrocarbyl, the substituent or substituents can be any group or groups which do not have an undesirable adverse effect on the antimicrobial activity of the biguanide such as a hydrocarbyloxy, hydrocarbylcarbonyl (i.e. acyl), an ester (i.e. acyloxy), halogen atom or CN.

The polymeric and oligomeric species of the PG contain a recurring unit represented by the formula



wherein X and Y may be the same or different and represent bridging groups in which the total number of carbon atoms directly interposed between the pairs of nitrogen atoms linked by X and Y is at least 9 and not more than 17.

The bridging groups X and Y may be polymethylene chains, optionally interrupted by hetero atoms such as oxygen, sulphur or nitrogen. X and Y may also incorporate cyclic nuclei which may be saturated or unsaturated, in which case the number of carbon atoms directly interposed between the pairs of nitrogen atoms linked by X and Y is taken as including the shortest segment or segments of the cyclic group or groups. Thus, the number of carbon atoms directly interposed between the nitrogen atoms in the group

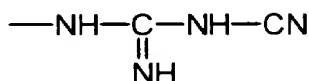


is 4 and not 8.

A preferred PG for use in the present invention is poly(hexamethylene biguanide), in which X and Y both represent a $\text{—(CH}_2\text{)}_6\text{—}$ group.

The PG may be prepared by the methods described in UK Patent Specification Nos. 702,268 and 1,152,243 respectively, and any of the polymeric or oligomeric biguanide species or mixtures thereof described therein may be used as the PG in the present invention.

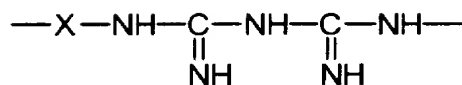
The PG may be terminated by an amine hydrochloride group or by an



group, and the terminating groups on each polymeric or oligomeric chain may be the same or different.

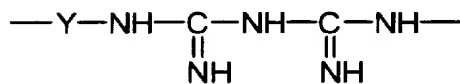
The number of individual biguanide units, i.e.

4



or

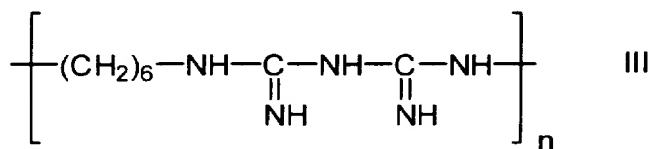
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in the PG is preferably from 2 to about 40.

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An especially preferred PG is a mixture of poly(hexamethylene biguanides) of formula III in the form of the hydrochloride salt.



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wherein n is from 1 to 40 having an average molecular weight from about 400 to about 11000.

A preferred PG is available as an aqueous concentrate supplied as VANTOCIL IB (ZENECA Ltd).

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The ABA may be any agent which reduces the substantivity of oligomeric biguanides for the cellulosic substrate and is preferably urea or an inorganic acid.

When the ABA is an inorganic acid, the acid should be sufficiently strong to increase the degree of protonation of the biguanide groups in the oligomers.

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Examples of suitable inorganic acids are hydrohalic acids such as hydrochloric acid and hydrobromic acids, nitric acid, sulphuric acid, phosphoric acid, pyrophosphoric acid, phosphonic acid, phosphonic acid ester, phosphoric acid ester or sulphonic acid.

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The phosphonic or sulphonic acid may be an optionally substituted aryl or optionally substituted alkyl phosphonic or sulphonic acid. The aryl group is preferably phenyl and the alkyl group is preferably C₁₋₆-alkyl and especially C₁₋₄-alkyl. Any substituents on alkyl or aryl should not significantly reduce the strength of the acid.

The phosphoric acid ester may be a mono- or a di-ester. It may be derivable from an optionally substituted phenol or optionally substituted alcohol. The optionally substituted alcohol preferably contains up to 6 carbon atoms and especially up

to 4 carbon atoms. Any substituent on the phenol or alcohol is as defined for sulphonic acid.

Preferred inorganic acids are hydrochloric and sulphuric acids.

When the ABA is an inorganic acid the treatment according to the present process is preferably followed by a thorough washing or neutralisation to remove excess ABA. It is therefore preferred that the ABA is urea because this avoids the need for such a post-treatment neutralisation or washing.

The amount of PG applied to the cellulosic substrate may be just sufficient to confer an antimicrobial effect to the substrate but is preferably in excess of this amount. Preferably the amount of PG is less than 2%, more preferably less than 1% and especially less than 0.5% based on weight of cellulosic substrate.

The PG can be applied to the cellulosic substrate by exhaust, dipping, padding or spraying or any other method known to the art. It is preferably applied from aqueous solution. The pH of the PG solution is preferably greater than 4 and especially greater than 6. It is also preferred that the pH of the PG solution is less than 12, more preferably less than 10 and especially less than 8.

Because PG exhibits high substantivity for the cellulosic substrate it is preferably applied at from 20 to 25°C.

The ABA is preferably applied from aqueous solution.

When the ABA is urea, it is preferably applied as a 1%, more preferably 2% and especially a 4% by weight solution. It is preferred that the amount of urea is less than 10% and especially less than 8% solution.

When the ABA is an inorganic acid it should be present in an amount to give a pH value below 2, more preferably below 1.5 and especially below 1.2.

The cellulosic substrate may be natural or regenerated cellulose and may be in the form of loose fibre, flock, pulp, thread or formed article. Particularly preferred forms of formed articles are woven and knitted piece goods and dry or wet laid fibres. The formed article may be an absorbent article such as a sponge or an article of clothing, towelling, drape or sheeting. Particularly important articles are those which may become soiled and susceptible to microbiological growth, thus giving rise to objectionable odours or health/hygiene problems. Specific examples of clothing are shirts, underwear, uniforms and socks.

The cellulose may be present in the cellulosic substrate on its own or may form a blend with a man-made polymer such as polyacrylamide, polyamide or polyester, particularly polyethyleneglycolterephthalate.

When the cellulosic substrate is in the form of flock or pulp, it may be a chemical pulp or thermo-mechanical pulp as is typically used in the absorbent layer of disposable items such as nappies, incontinence pads and feminine hygiene packs.

When the cellulosic substrate is treated with PG in aqueous solution the various oligomers are all retained substantively by the cellulose and there is no differentiation between the oligomers of high and low molecular weights i.e. the oligomers of PHMB of formula III wherein n is from 1 to 40 are absorbed and retained by the cellulose to a similar extent. When the PG containing cellulosic substrate is treated with an ABA low molecular weight oligomers such as PHMB of formula III wherein n is from 1 to 5 and preferably when n is from 1 to 7 are removed together with some by-products arising from the manufacture of the PHMB.

Thus, according to a further aspect of the invention there is provided a cellulosic substrate containing PHMB which consists substantially of oligomers of formula III wherein n is from 5 to 40 and especially from 7 to 40.

As noted hereinbefore, the PG confers antimicrobial properties to the cellulosic substrate and the removal of low molecular weight oligomer biguanide species from the treated cellulose has no significant effect on the anti-microbial properties of the treated cellulosic substrate.

The PG may be the only antimicrobial agent applied to the cellulose. However, the cellulosic substrate may also contain other antimicrobial agents if it is desired to improve the spectrum of micro-biological activity. Such other antimicrobial agents should not significantly interfere with the improved resistance to yellowing in the presence of hypochlorite which has been conferred to the cellulosic substrate by removing the low molecular weight oligomeric biguanide species.

When the cellulosic substrate is in the form of textile material it may contain any of the normal adjuvants which are used in textile finishing such as dyestuffs, softeners, optical brighteners and binders or resins which are commonly used to impart an "easy-care" finish.

The application of the PG to the cellulosic substrate and treatment with ABA preferably occurs as the final stage in any finishing operation but can clearly be incorporated with any prior finishing process as appropriate. In the case of textile materials which contain an "easy-care" finish the application of the PG and treatment with ABA preferably precedes the application of the finish.

The invention is further illustrated by the following examples wherein all references are to parts by weight unless indicated to the contrary.

Example 1

Bleached Indian head cotton piece (0.2 parts, 5cm²) was immersed in 3ml of a 0.4% by weight aqueous solution of PHMB at pH 7-8 at 20-25°C for 20 minutes. The cotton piece was then removed and the residual PHMB solution examined by Size Exclusion Chromatography (SEC) equipped with a silica column which was developed with an aqueous solution of methanol, ammonium chloride and hydrochloric acid. The various oligomers of PHMB were detected by UV absorption at 220 nm.

The residual PHMB solution was compared with an original sample of 0.4% PHMB to which no cotton had been added. Comparison of the chromatographs showed them to be identical in that both contained the full gamut of oligomers indicating the oligomeric distribution was not altered by adsorption onto cotton and that no preferential absorption of particular oligomeric fractions of PHMB had occurred. In both instances the weight average molecular weight was about 2800.

Example 2

A sample of cotton containing PHMB was prepared as described in Example 1. After removing from the PHMB solution it was rinsed and dried and then immersed in 10ml of distilled water at 80°C for 20 minutes. The cotton sample was then removed and the oligomeric content of the water determined as before by SEC. This indicated that a small amount of low molecular weight oligomers was removed with an average molecular weight of about 700. i.e. n is about 3 to 4 for PHMB of formula III.

Example 3

Example 2 was repeated except that the distilled water was replaced by a 1% aqueous solution of sulphuric acid. Evaluation of this sulphuric acid solution by SEC showed that more oligomeric PHMB was removed and that this corresponded to mainly low to mid molecular weight range of oligomers with average molecular weight of about 1000 to about 1250. This corresponds to n of from 1 to 5 and n of 1 to 7 in the PHMB of formula III.

Example 4

Indian head cotton piece (10 parts) was passed through an aqueous solution of 0.2% PHMB and squeezed through nip rollers to give 50% pick-up on weight of dry cotton.

A dried sample of treated cotton (0.2 part) was then immersed in 3 mls of a 1% sulphuric acid at a pH of approximately 1, rinsed with water and again dried. This cotton sample was then immersed in 3mls of a 3% aqueous solution of sodium hypochlorite at 40°C for 1hr. It was then removed, squeezed, rinsed in water and dried.

The colour of the treated cotton was assessed visually by measuring with a Macbeth Reflectance Spectrophotometer and compared with an untreated piece of cotton and also cotton treated with the same amount of PHMB which had not been acid rinsed.

The results are given in Table 1 below which show that the yellowing of PHMB treated cotton is mainly due to low to mid molecular weight oligomers of PHMB i.e. n is approximately 1 to 5 for PHMB of formula III.

TABLE 1

Cotton treated	Whiteness (%)	Visual appearance
0.1% PHMB	70.7	Yellow
0.1% PHMB then 0.1% Sulphuric acid	96.7	White
Control	97.5	White

Example 5

Samples of cotton (0.5 parts) were treated with a 0.4% by weight solution of PHMB as described in Example 1. Samples before and after extraction with 0.1% sulphuric acid were incubated in 5 parts perspiration liquor for 4 hours at 37°C. Both an acid perspiration (pH 5.5) and alkaline perspiration (pH 8) were evaluated using the perspiration recipes and methodology set fourth in BS 1006, May 1983.

The PHMB content of the perspiration liquors was determined by a colorimetric method involving reaction with Eosin and measuring the optical density at 545nm. The results are given in Table 2 below which show that some of the oligomers of PHMB are extracted into the perspiration liquor but that following acid extraction whereby the low to medium oligomers of PHMB are removed, no PHMB is extracted.

Slightly more oligomeric PHMB is extracted into the acid perspiration than the alkaline perspiration liquor.

TABLE 2

Cotton treatment	Perspiration (pH)	PHMB extracted
0.4% PHMB	5.5	78
	8	58
0.4% PHMB then 0.1% Sulphuric acid	5.5	<1
	8	<1
Control	5.5	2
	8	<1

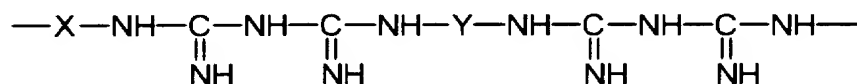
Example 6

Example 3 was repeated except that the 0.1% sulphuric acid solution was replaced by an aqueous solution containing 20 parts/litre urea and a synthetic urine also containing the same amount of urea. These urea solutions were also analysed by SEC and the oligomeric PHMB fraction extracted by these urea solutions was found to be very similar to that extracted by the 0.1% sulphuric acid solution.

CLAIMS

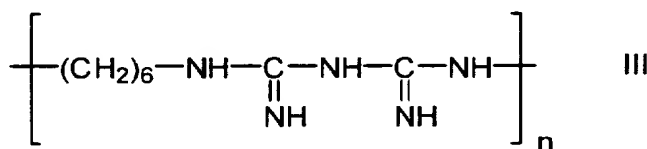
1. A method for treating a cellulosic substrate with a polymeric biguanide and thereafter treating the cellulosic substrate containing the polymeric biguanide with an anti-bonding agent.

2. A method as claimed in claim 1 wherein the polymeric biguanide contains polymeric and oligomeric species with a recurring unit represented by the formula



wherein X and Y may be the same or different and represent binding groups in which the total number of carbon atoms directly interposed between the pairs of nitrogen atoms linked by X and Y is at least 9 and not more than 17.

3. A method as claimed in either claim 1 or claim 2 wherein the polymeric biguanide is a mixture of poly(hexamethylene biguanides) of formula III in the form of the hydrochloride salt.



wherein n is from 1 to 40.

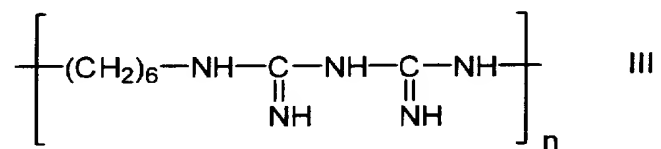
4. A method as claimed in one of claims 1 to 3 wherein the anti-bonding agent is urea.

5. A method as claimed in one of claims 1 to 3 wherein the anti-bonding agent is an inorganic acid.

6. A method as claimed in claim 5 wherein the inorganic acid is present in an amount to give a pH value below 2.

7. A method as claimed in any one of claims 1 to 6 wherein the cellulosic substrate is thoroughly washed to remove excess antibonding agent.

8. A cellulosic substrate containing poly(hexamethylene biguanide) which consists substantially of polymers and oligomers of formula III



wherein n is from 5 to 40.



Application No: GB 9608073.4
Claims searched: 1-8

Examiner: Peter Davey
Date of search: 3 July 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.O): D1P (PCBA), A5E (ECA, EN, ET)
Int Cl (Ed.6): D06M 11/11 11/55 13/432, A01N 47/44
Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
P,X	WO 95/12021 A1 (ZENECA), 4 May 1995, see eg. page 1, lines 1-4 and 26-33, page 4, lines 1-7 and page 6, lines 36-40	1 and 8 at least
X	EP 0136900 A1 (SURGIKOS), see eg. page 6, lines 7-9 and page 7, lines 10-20	8

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.